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# Effect of Cu for Mn on the magnetic properties of Mn-Zn ferrites

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**Abstract** : The effect of $Mn^{2+}$ substitution for $Cu^{2+}$ ions in the magnetic properties of iron-excess Mn-Zn ferrites $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ with $x$ = 0.0, 0.06, 0.10, 0.15 have been investigated. X-ray analysis indicates the formation of single phase cubic spinel structure for all values of $x$. The bulk and X-ray density increases whereas porosity decreases with increased value of $x$. The saturation magnetization seems to decrease with increasing value of $x$. The Curie temperature shows a decreasing trend for the increased substitution of $Cu^{2+}$ ions. The real part of the complex permeability is found to increase as Cu content increases.

**Keywords** Ferrite; magnetization; magnetic permeability

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High resistivity, stability and moderate cost of ferrites have made them attractive in a wide range of technological applications in radio frequency devices, high quality filters, and transformer cores [1]. Mn-Zn ferrites have drawn interest as soft magnetic materials for high frequency applications due to their lower losses at high frequency in comparison with Ni-Zn ferrites. High magnetic permeability, high resistivity and lower eddy current losses allow their use to higher frequencies. The properties of the ferrites can be modified by substitution [2,3] or addition and also by controlling the sintering temperature. In the present work, the influence of Cu as substitute for Mn on the properties of Mn-Zn ferrites have been investigated by studying lattice constant, density, porosity, magnetization, Curie temperature, frequency dependence of initial permeability and loss tangent.

The samples of $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$, with $x = 0.0, 0.06, 0.10, 0.15$ were prepared by the standard ceramic method. The chemicals MnO, CuO, ZnO and $Fe_2O_3$ used were of analytical research grade supplied by E. Mark of Germany. The mixing, grinding, pre-sintering and sintering procedure were same as described elsewhere [4]. Four sets of samples were prepared by sintering at four different temperatures of 1188°C, 1241°C, 1288°C, 1365°C within an accuracy of ±1°C. At first, the temperature was raised to 200°C at the rate of about 5°C/min and then to 600°C in 60 minute. Then, the temperature was raised to the desired firing temperature and kept at this temperature for 2 h. After that the furnace was slowly cooled to 600°C in 2 h and then switched off for natural cooling. Another set of samples were heated to 1300°C and instead of slow cooling, were quenched directly to room temperature. Samples sintered at 1288°C were used for X-ray investigation. The diffractogram indicated the single phase spinel structure formation. The lattice constants were calculated from the diffraction angle. Magnetization of the samples were measured at room temperature by a Foner type vibrating sample magnetometer. Curie temperatures were determined from the temperature dependence of initial permeability. At the ferrimagnetic transition temperature $T_c$, the initial permeability drops substantially. Frequency dependence of initial permeability and loss tangents of the toroid samples were measured with the help of an Impedance analyzer ( HP4192A) in the frequency range 10KHz to 10MHz.

The X-ray diffraction patterns for all the samples displayed the fundamental peaks of single-phase cubic spinels, essentially matching with that of $ZnFe_2O_4$ ( Franklinite JCDPS No. 22-1012) and Ni-Zn ferrite reported by Chatterjee *et al* [5]. The physical

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properties such as lattice constant (a), bulk density ($\rho_B$), X-ray density ($\rho_x$) and porosity ($P$) were calculated using the X-ray data and are summarized in Table 1.

Figure 1 shows the magnetization, $M$ *versus* magnetic field, $H$ curves for samples containing various amount of $Cu^{2+}$ of the compositions $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ sintered at 1288°C. It

**Table 1.** Parameters of $Mn_{0.7-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ with $x$ = 0.0, 0.06, 0.10 and 0.15.

| Samples | Sintering temperature | a (Å) | $\rho_x$ (gm/cm$^3$) | $\rho_B$ (gm/cm$^3$) | Porosity P (%) | $M_S$ (emu/gm) | $T_c$ (°C) |
|---|---|---|---|---|---|---|---|
| $x$=0.0 | 1288°C | 8.528 | 4.992 | 4.686 | 6.129 | 78.980 | 297 |
| $x$=0.06 | 1288°C | 8.510 | 5.035 | 4.786 | 4.945 | 68.983 | 255 |
| $x$=0.10 | 1288°C | 8.526 | 5.012 | 4.802 | 4.189 | 76.631 | 237 |
| $x$=0.15 | 1288°C | 8.514 | 5.042 | 4.776 | 3.275 | 76.096 | 242 |

The bulk density $\rho_B$, was measured by usual mass and dimensional consideration whereas X-ray density, $\rho_x$, was calculated using the expression [6]

$$\rho_x = \frac{ZM}{NV},$$

where $M$ is the molecular weight, $N$ is the Avogadro's number, $V$ is the volume of the cubic unit cell and $Z$ is the number of molecules per unit cell, which is 8 for the spinel cubic structure. The porosity $P$ of the samples were calculated from $\rho_B$ and $\rho_x$ values using the expression [7]

$$P = 1 - \frac{\rho_B}{\rho_x}.$$

The effect of $Cu^{2+}$ ion substitution on the bulk and X-ray densities ($\rho_B$, $\rho_x$) and on the porosity $P$ is shown in Table 1. The bulk density is lower than the X-ray density. This may be due to the presence of pores, which were formed and developed during the sample preparation and the sintering process. It is evident from Table 1 that the substitution of $Cu^{2+}$ increases $\rho_x$ and reduces $P$ of the samples. The increase in density with $Cu^{2+}$ substitution in Mg-Zn ferrites has also been reported by Rezlescu *et al* [8]. The density increase is caused by the lowering of the porosity and by the segregated layer. The reduction of $P$ may be for that the presence of $Cu^{2+}$ helps the intergranular pores to move to the grain boundaries to a certain extent.

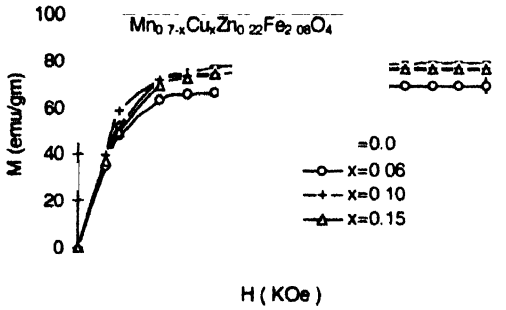


**Figure 1.** Field dependence of magnetization $M$ of $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ sintered at 1288°C.

can be seen that the saturation magnetization measured at room temperature of 300K varies with the substitution. The variation of the saturation magnetization, $M_S$, as a function of concentration of $Cu^{2+}$ ions is shown in Figure 2. It indicates a decrease of $M_S$ value with addition of $Cu^{2+}$ ions. The decrease

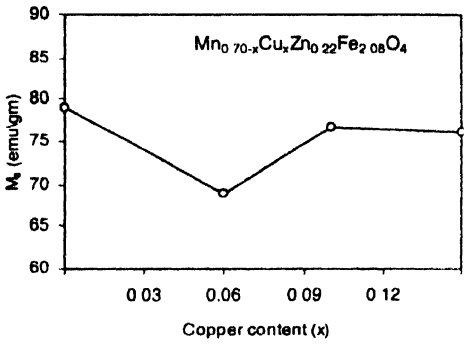


**Figure 2.** Variation of saturation magnetization $M_S$ with Cu-content $x$ in $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$.

in magnetization with copper content $x$ may be explained by taking into account the cation distribution in the ferrite. Neutron diffraction studies of $Mn_{0.60}Zn_{0.40}Fe_2O_4$ ferrite [9] suggested the cation distribution as :

$$\left[Mn^{2+}_{0.60}Zn^{2+}_{0.40}\right]_A \left(Fe^{3+}_2\right)_B O$$

This shows that all the $Mn^{2+}$ and $Zn^{2+}$ ions occupy tetrahedral $A$-sites while all the $Fe^{3+}$ ions occupy octahedral $B$-sites. It has also been reported that $Cu^{2+}$ ions have strong preference for the octahedral $B$-sites [10]. Considering the preference of site occupation and the charge neutrality, the cation distribution in $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ can be assumed as

$$\left[Mn^{2+}_{0.70-x}Zn^{2+}_{0.22}Fe^{2+}_{0.08}Fe^{3+}_x\right]_A \left(Cu^{2+}_x Fe^{3+}_{2-x}\right)_B O^{2-}_4.$$

*i.e.* for $x$ = 0, the site occupancy is assumed as

$$\left[Mn^{2+}_{0.70}Zn^{2+}_{0.22}Fe^{2+}_{0.08}\right]_A \left(Fe^{3+}_2\right)_B O^{2-}_4.$$

By substituting $Mn^{2+}$ ions with $Cu^{2+}$ (which have a magnetic moment of 1 $\mu_B$), a decrease in the magnetization $M_B$ of $B$-site

takes place and due to the migration of $Fe^{3+}$ ions from *B* to *A* site, an increase in the magnetization $M_A$ of *A*-site occurs leading to a net decrease in the magnetization $M_S$ (= $M_B - M_A$). Thus, the decrease in saturation magnetization with the increased Cu content of $x = 0.06, 0.10, 0.15$ can be explained.

Curie temperature ($T_c$) has been estimated from the initial permeability ($\mu$) *vs* temperature ($T$) curves for the different Mn-Zn ferrite samples. At Curie temperature $T_c$, the permeability $\mu$ showed abrupt fall (Figure 3). For larger copper content, $\mu$ increases, but the plateau in the $\mu - T$ curves narrows. Similar phenomena were observed by Rezlescu *et al* [8] for copper substitute Mg-Zn ferrite. The Curie temperature shows an

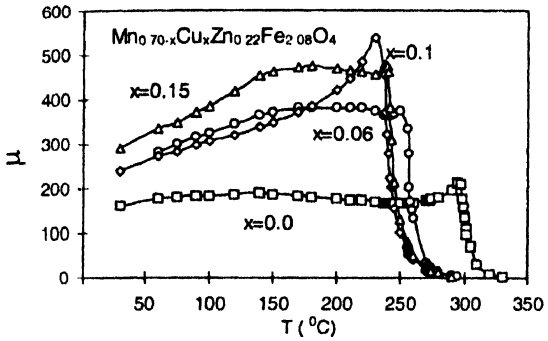


Figure 3. Curie temperature determination from the temperature dependence of initial permeability $\mu$ of $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ sintered at 1288°C

expected decreasing trend on substitution of non-magnetic $Cu^{2+}$ ions for $Mn^{2+}$ ions (Figure 4). This decrease of the Curie temperature with increasing $Cu^{2+}$ content may be due to the weakening of the A–B exchange interaction strength due to the change of the Fe distribution between *A*-and *B*- sites.

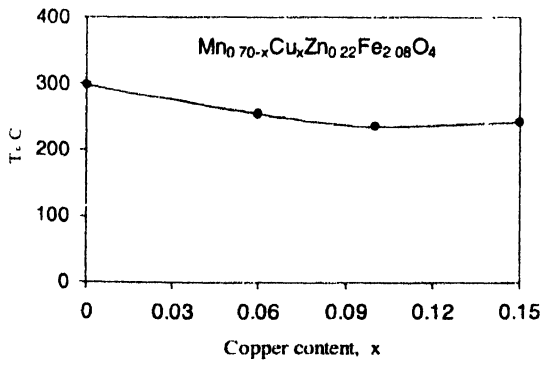


Figure 4. Variation of Curie temperature $T_c$ with Cu-content x in $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ sintered at 1288°C.

The frequency-dependence of the real part of complex permeability is shown in Figure 5. For Mn-Zn ferrites to be used as core materials, the real part $\mu$ of the complex permeability should remain fairly constant over certain frequency range. The flat region up to the frequency of 2 MHz, indicates that all the samples having different compositions are suitable as core materials at low field. Above 2 MHz, the real part of the permeability decreases. Figure 5 shows the permeability values with increasing copper content. From Table 1, it is evident that the increase in $x$ (copper content) decreases the porosity in the samples. Thus, permeability appears to increase as the porosity decreases. It is observed that the highest value of initial permeability of 359 is attained for sample with 0.15 mole % Cu content that has the lowest porosity. In order to obtain higher permeability, it is necessary that the specimen should have as few pores as possible[11].

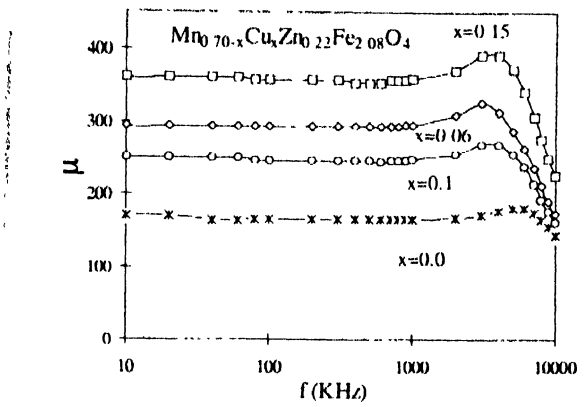


**Figure 5.** Frequency dependence of the initial permeability $\mu$ of $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ with $x$ = 0.0, 0.06, 0.10, 0.15 sintered at 1288°C.

Figure 6 shows the curves of $\mu$ against frequency for the samples sintered at four different temperatures of 1188°C, 1241°C, 1288°C, 1356°C along with that of the sample quenched from 1300°C. With the increase of sintering temperature $T_s$, $\mu$ is found to increase up to 1288°C. This result is supported by Pankert [12]. All the samples except that treated at 1365°C, shows this expected increase in permeability. For the sample heat-treated at 1365°C, the permeability was found to decrease significantly. This we believe, is due to the reason that the sample heat-treated at higher temperature, contains increased number of pores within the grains, which resulted in sharp decrease of permeability. Similar phenomena were observed by Guillaud [13]. He demonstrated that the permeability of a Ni-Zn ferrite drastically decreased with increasing percentage of grains possessing pores despite increasing grain size. However, the samples

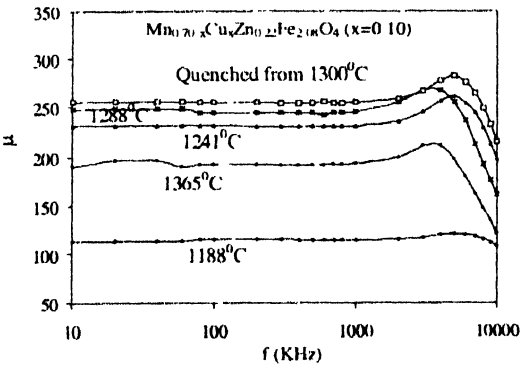


**Figure 6.** Effect of sintering temperature on the initial permeability $\mu$ of $Mn_{0.70\,x}Cu_xZn_{0.22}Fe_{2.08}O_4$ for $x$ = 0.10 sintered at different sintering temperatures.

'quenched' from 1300°C to room temperature, give the highest value of permeability. The grain size of the quenched samples was found to be smaller compared to the slow cooling ones and the grains were also uniform. This we believe, is due to the reason that the grains did not get sufficient time to grow. When the materials are quenched from an elevated temperature, the condition of the samples at the elevated temperature is normally 'frozen in'. As a result, uniformly distributed and microscopically more homogeneous materials with smaller grains and lower porosity were obtained. Smaller and uniform grains with lower porosity are expected to give a higher value of permeability. Thus, a higher value of $\mu$ for quenched materials can be accounted.

Figure 7 represents the loss tangent $\tan\delta$, of Mn-Zn ferrites with different percentage of Cu substitutions in the frequency range of 10KHz to 10MHz. The $\tan\delta$ value is found to decrease with the increased content of copper. It is observed that $\tan\delta$ is minimum for frequency up to 2 MHz and then begins to rise. The loss tangent is attributed to various domain defects [14] which include non-uniform domain wall motion, localized variation of flux density and nucleation and annihilation of domain walls. The rise in the value of $\tan\delta$ beyond the frequency of 2MHz can be associated with the ferrimagnetic resonance [15].

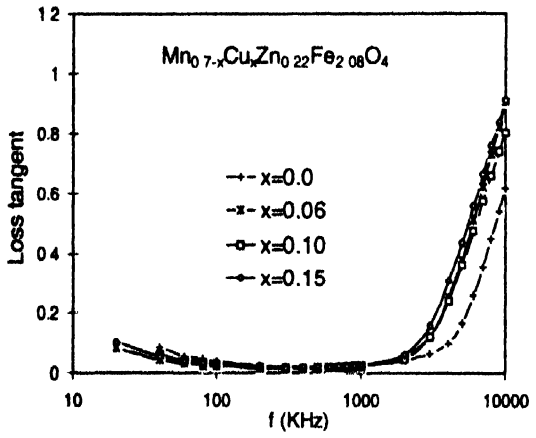


**Figure 7.** Frequency dependence of loss tangent of $Mn_{0.70-x}Cu_xZn_{0.22}Fe_{2.08}O_4$ sintered at 1288°C.

In conclusion, it can be said that Cu-substitution enhances the density and reduces the porosity of the samples. With the Cu-substitution, the saturation magnetization decreases with copper content. Curie temperatures show a decreasing trend with the copper substitution. With the increasing concentration of Cu *i.e.* with decrease in porosity, the initial permeability of the samples shows an increasing tendency. Higher concentration of Cu reduces the loss tangent as it improves the quality factor of the samples. Quenching from elevated temperature yield samples with higher value of permeability. Thus, it may be said that Cu-substitution increases the densification and reduces the porosity of the Mn-Zn ferrite samples and as a consequence improves the magnetic properties of these ferrite samples

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